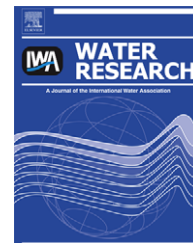


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Impact of sewage sludge conditioning and dewatering on the fate of nonylphenol in sludge-amended soils

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ABSTRACT

The fate of ¹⁴C-labelled p353-nonylphenol (NP) in soils amended with differently treated sludges originating from the same precursor sludge was assessed. The effects of commonly applied conditioning and dewatering techniques were investigated. Nonylphenol was degraded considerably faster in soils amended with liquid sludge, while a significant portion of it remained intact and extractable by organic solvents when sludge had been centrifuged before soil amendment. Mineralization was reduced or even inhibited when freeze-thaw or lime conditioning was applied, respectively. Flocculation by an acrylamide-based cationic polymer led to the formation of a nitro-addition product of nonylphenol in soil, as well to decreased mineralization rates after prolonged incubation times. Possible mechanisms underlying the observations are suggested and discussed.

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1. Introduction

Improved standards in wastewater treatment worldwide have resulted in new installations and extension of the existing facilities, thus leading to an increase in wastewater sludge production. Although the use of sludge fertilizer in agriculture still accounts for a significant proportion of the total municipal sludge disposal in many countries (Spinosa, 2007), concerns on the possible risks – derived from the presence of pathogens, heavy metals and organic pollutants in sludge (Harrison et al., 2006) – tend in some cases to decrease the agricultural use in favor of incineration. In North Rhine-Westphalia, the most populated Federal State in Germany, the part of

municipal sludge used for agricultural purposes was decreased from 33% in 2000 to 22% in 2005, while in the same period the incineration proportion climbed to 64% from 39% in 2000 (LANUV-NRW).

In the future it is expected that only good quality sludge will be amended on agricultural soils. Within EU, the Directive 86/278/EEC, currently under revision, sets tolerance values for heavy metals in sewage sludge and soil (CEC, 1986). Providing limit values also for organic pollutants in sludge is under consideration (Abad et al., 2005). However, great uncertainties in fate processes in soil need to be resolved, before risk assessment models could produce secure tolerance values (Schowanek et al., 2004).

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The fate of an organic chemical in a sludge-amended soil depends on soil parameters, sludge characteristics, environmental conditions, as well as agricultural practices. Since the sludge matrix comprises the direct environment of sludge pollutants in soil, sludge is expected to have a considerable influence on the mobility and the biological degradation of contaminants. Sludge composition may be highly variable, according to its origin and type (geographical and seasonal, municipal or industrial, etc.) and the treatment it has been posed to. Studies on the role of sludge origin (Dubroca et al., 2005) and sludge stabilization (Hesselsøe et al., 2001; La Guardia et al., 2001; Mortensen and Kure, 2003; Xia and Jeong, 2004) on the fate of organic pollutants in soil have been reported. However, the role of further sludge treatment processes has not been investigated yet. As the sludges used in the mentioned studies were sampled from different plants or process units, comparisons between the various studies are difficult due to the fact that different treatments were applied and sludges of different origins were used.

In the present study the role of sludge treatment in the fate of organic contaminants in sludge-amended soils is investigated by applying different treatments on the same precursor sludge. The work is focused on the last steps of sludge treatment processing, which are usually conditioning and dewatering.

Sludge dewatering is often necessary for agricultural use, since this step of sludge treatment contributes to cost savings in transport and disposal. Commonly employed techniques are cake filtration, centrifugation, and bed drying (Dirkzwager and Hermite, 1988). Conditioning allows for the enhancement of sludge's water removal efficiency. It is most often performed through addition of chemical additives, like ferric chloride, lime (CaO) and organic polymers (predominantly cationic). By addition of chemicals, flocculation of the sludge is actually achieved. Physical conditioning methods are also applied; among them, freeze-thaw conditioning appears to be the most promising alternative to chemical treatment (Dentel, 2001). This method relies on the fact that freezing water excludes solid particles ahead of the advancing ice front (Tao et al., 2006).

Freeze-thawing and liming of sludge have been shown to increase the persistence of a model organic pollutant, i.e. p353-nonylphenol (NP), spiked on soil-sludge mixtures (Kouloubos et al., 2008). According to this study, conditioning of sludge with cationic polymer was suspected to slightly decrease the leaching potential of NP, while liming would increase leaching.

In the present study, the impact of commonly applied conditioning and dewatering methods on the fate of p353-NP in sludge treated soil is investigated. NP was directly spiked to the liquid sludge before the application of the different sludge treatment methods, which afterwards was amended to the soil. Such strategy allows, in comparison with a homogeneous spiking on the sludge-amended soil (Kouloubos et al., 2008), a better simulation of the agricultural fields, where the organic contaminants enter in fact as a component of the sewage sludge. The results are reported for each sludge treatment technique and possible mechanisms underlying the observations made are suggested and thoroughly discussed.

2. Experimental

2.1. Synthesis of ^{14}C -labelled p353-nonylphenol

[ring- ^{14}C]-p353-nonylphenol (4-[1-ethyl-1,3-dimethylpentyl] phenol) was synthesized by Friedel-Crafts alkylation (Vinken et al., 2002). The identity of the synthesized compound was certified by GC/MS and its purity grade was 97%, as determined by HPLC coupled to radiodetection (see below). The specific radioactivity was 883 Bq/ μg .

2.2. Spiking and treatment of sewage sludge

Liquid mesophilic-anaerobically digested and thickened sludge (dry matter, DM: 4.8%, organic matter: 47% of DM) was sampled from Soers municipal Wastewater Treatment Plant (WWTP) in Aachen, Germany. Sludge aliquots (24 g each) were poured in glass centrifugation tubes and spiked with 230–239 μg of [ring- ^{14}C]-p353-nonylphenol using approximately 150 μL of a concentrated solution in ethanol. The liquid sludges were then conditioned by means of four different methods. Three chemical treatments (percentage expressed in relation to the dry matter of sludge), i.e. 8% FeCl_3 , 8% $\text{FeCl}_3 + 26\%$ $\text{Ca}(\text{OH})_2$, and 0.5% cationic polymer [NEROLAN CE 679 S, Nerolan Wassertechnik GmbH Krefeld, a donation from Soers WWTP] and one physical treatment (freeze-thaw: freezing at -21°C for 48 h, thawing at room temperature) were used. The chemical conditioning doses correspond to average doses used in WWTPs (Ivashechkin et al., 2004). Mixing with the conditioning agents, which were added in the form of aqueous solutions (FeCl_3 , 10%; $\text{Ca}(\text{OH})_2$, 20% and polymer, 0.7% by weight), was performed under shaking for 30 min at 180 rpm. The conditioned sludges were centrifuged for 60 min at 16,000g (J-21C centrifuge, Beckman, Munich, Germany). After centrifugation, the radioactivity was determined by means of liquid scintillation counting (LSC, see below) in 1 mL aliquots of the supernatants prior to the removal of the liquid phase. The expected amount of losses of NP through the sludge processing was determined during a preliminary test carried out under strictly identical conditions. The exact amount of NP spiking was based on these results, in order to obtain dewatered sludges containing the same final amount of NP. During an additional preliminary test, the possibility of an early transformation of NP during liming (pH of limed liquid sludge: 11) was investigated by extracting treated sludge and analyzing the extract by HPLC. Each spiking/treatment protocol was applied in triplicate. Three further sludge samples after spiking were dewatered without any prior conditioning (conditioning control). Finally, three smaller aliquots (2.5 g) were spiked, but not dewatered (dewatering control).

2.3. Amending of sludges to soil and incubation

Samples (13 g each) from an air-dried and 2 mm-sieved standard soil (loamy sand, organic C: 2.3%, pH: 5.7, Water Holding Capacity, WHC: 48 g/100 g, LUFA Speyer, Speyer, Germany) were poured in glass tubes, irrigated with 1 mL of water and incubated in the dark under thermostated (20°C) and

continuous aeration (with air saturated in water) conditions in flow-through systems (Telscher et al., 2005) for one week. Afterwards, the radioactive sludges were amended gradually on wet soil samples and the mixtures were homogenized with a spatula. One milliliter of water was added again to each system (except the soils amended with liquid sludge) and homogenization was repeated. The humidity of the soil-sludge mixtures was set to 65% and 73% of their WHC for dewatered and liquid sludge amendments, respectively. At the end, a slight pressure was exerted on the top of the sludge-amended soils, in order to produce similar oxygen penetration profiles for all soils. The amounts of radioactivity lost during the amending procedure (residues on centrifugation tubes, spatula and flattening tool) were determined by using adequate protocols (extraction with ethanol, catalytic combustion and LSC). The soil-sludge mixtures were connected again to the flow-through systems, where they were incubated for 87 d.

2.4. Determining the fate of NP in sludge-amended soils

2.4.1. Mineralization of NP

During incubation, the mineralization course of radioactive NP was determined by trapping the evolved CO₂ in flasks containing 50 mL 2 M NaOH. One milliliter aliquots from the NaOH solution were sampled at various time points of incubation for measurement of radioactivity assignable to ¹⁴CO₂ (LSC).

2.4.2. Extractable residues of NP and degradation products

After homogenization, 5 g wet aliquots from the incubated sludge-amended soils were extracted sequentially with acetone (25 mL, 5 min shaking at 180 rpm), *n*-hexane (25 mL, 40 min shaking), methanol (25 mL, 40 min shaking), NaOH 0.1 M (twice, 25 mL, 40 min shaking), and methanol (25 mL, vortex shaking for 15 s). The recovery of NP from freshly spiked soil-sludge mixtures was determined to be 98.8–99.2% (recovery range of a triplicate preliminary test). Extraction by acetone served also as a drying step, and the dry mass of the soil-sludge aliquots was determined before *n*-hexane extraction, after evaporating remaining acetone under a stream of N₂ (although acetone removes except water also part of the organic matter, the error induced by determining the dry mass by this method was measured to be negligible, data not shown). After each extraction step the slurries were centrifuged (3500 g, 10 min) and the radioactivity was determined in 1 mL of the supernatants using LSC before pooling the organic extracts and alkali solutions separately. The organic extracts were first filtered under vacuum through 15 g of Na₂SO₄ (over glass wool) and then through a paper filter. Afterwards they were concentrated in a rotary evaporator (40 °C, 100 mbar). The concentration of NP and degradation products was determined in the concentrated extracts using HPLC coupled to a radiodetector. The NaOH extracts were used for the analyses of bound residues (described below).

2.4.3. Leaching potential of NP and degradation products

Two grams of aliquots from the incubated sludge-amended soil were subjected to a modified version of the U.S.

Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP, SW-846, EPA Method 1311). Extraction was performed using an aqueous solution (40 mL) containing NaOH (0.13 M) and acetic acid (0.19 M) (pH ~ 5) under gentle shaking (80 rpm) for 10 h. The radioactivity contained in 1 mL sample of the extract (after centrifugation, 3500 g, 10 min) was measured by LSC. The leachate extract was later extracted by means of liquid–liquid extraction with ethyl acetate (30 mL, 5 min shaking at 80 rpm). After centrifugation (3500 g, 5 min), the two phases were separated. The ethyl acetate phase was further processed using filtration through 15 g Na₂SO₄, concentration in a rotary evaporator, drying under gentle stream of N₂, and resuspension to 300 µL of methanol, followed by HPLC analyses.

2.4.4. Bound residues

Under the extraction conditions applied, NaOH extracts contain the majority of the residues bound to the humic and fulvic acids of the soils (Romaris-Hortas et al., 2007). The extracts were firstly extracted using ethyl acetate (twice, 25 mL, shaking for 5 min at 80 rpm), to obtain the physically bound (entrapped) NP residues. The radioactivity of the organic ethyl acetate phase was measured by means of LSC (1 mL aliquot). The remaining NaOH phase was further fractionated by acidifying to pH < 1 with HCl 3 M, in order to separate precipitated humic acids (HA) from the soluble fulvic acids (FA). The radioactivity of the supernatant containing the fulvic acids fractions was measured by LSC.

After sequential extraction the soils were air dried before taking samples to determine the radioactive residues bound to humin and minerals. At this stage the soil consisted of two fractions, i.e. a dark brown elastic layer, which is hereafter referred to as humin fraction and a light colored sandy material, the minerals fraction. The two fractions were separated manually and 0.2–0.3 g aliquots were analyzed by catalytic combustion and subsequent LSC measurement.

2.5. Analytics

2.5.1. GC, LSC, Catalytic combustion, HPLC

GC/MS analysis was performed on an HP 5890 Series II gas chromatograph coupled with an HP 5971A mass selective detector (Hewlett Packard, Palo Alto, CA, USA) with an Electron Ionization source. The gas chromatographic analysis was performed with an FS-Supreme-5 silica capillary column (l = 30 m, i.d. = 0.25 mm, f.t. = 0.25 µm; Chromatographie Service, Langerwehe, Germany). The injector temperature was 250 °C, and the detector temperature was set at 280 °C. The oven program was 5 min at 50 °C and 10 °C/min to 280 °C (5 min). LSC and catalytic combustion of solid samples were carried out as described elsewhere (Corvini et al., 2004). Analysis on an HPLC system coupled to liquid scintillation-radiodetection was performed using a Nucleosil C18 reverse phase column and acetonitrile/water as mobile phase (Cirja et al., 2006).

2.5.2. Mass balance

Radioactivity values given in the paper are normalized, i.e. expressed in percent of the radioactivity recovered in each system (sum of mineralized NP, extractable and bound

residues fractions). The average recovery was 100% for the 18 sequential extraction samples (six differently treated sludges in triplicates) and for the 18 leaching potential extraction samples, denoting that any recovery deviations for single samples were presumably due to the sampling procedures.

3. Results

3.1. Fate of NP during sludge treatment

The losses of NP due to partitioning to the water phase that was removed after centrifugation, as well as the dry matter content of the dewatered sludges are summarized in Table 1. Only small amounts of NP were eliminated during sludge dewatering treatment, i.e. maximum of 1.3% in the case of limed sludge. The biosolids produced had a dry matter content similar to that of sludges produced in WWTPs. HPLC analysis of an extract of the limed sludge, in the frame of preliminary experiments, showed that no chemical transformation of NP could take place under these conditions (data not shown). On the basis of data collected during the sludge preparation, sludge treatment and soil amendment processes, the dewatered sludges were loaded with radiolabelled NP at 170–250 mg/kg (DM) at a sludge to soil ratio of approximately 1:10 (on DM basis). For the liquid sludges the level of spiked NP was 1850–1900 mg/kg (DM), while the respective mixture ratio was approximately 1:100 (for the relevance of comparing liquid and dewatered sludge amendments at this study, see Section 4).

3.2. Fate of NP in sludge-amended soils

3.2.1. Mineralization of NP

The mineralization of NP in sludge-amended soils is presented in Fig. 1. The amount of mineralized NP after 87 d of incubation was very low, not exceeding 7% of the spiked amount in any of the amended soils. Significant differences between the various treatment methods were observed. The

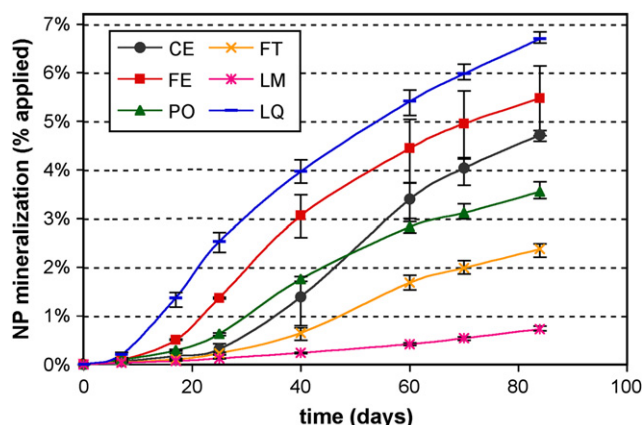


Fig. 1 – Mineralization of the phenolic ring of NP in soils amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge.

decomposition process was considerably slow when sludge had been freeze-thawed and negligible (only 0.7% had been transformed to ¹⁴CO₂) in the soil amended with limed sludge. The lag-period lasted ca. 15 d for all dewatered sludges, but only 5 d for the liquid sludge, in the matrix of which NP exhibited also the highest mineralization rate.

3.2.2. NP extractable by organic solvents

Analysis of the soils amended with dewatered sludges revealed that 87 d after spiking most of NP was intact and extractable with organic solvents (Fig. 2a). Particularly the NP levels in the soils amended with freeze-thawed sludge were slightly higher than in soils where differently treated dewatered sludges were applied (73–79% of the applied amount, in comparison with 65–73% in the 12 systems corresponding to the rest cases). When liquid sludge was used, the amount of NP that could be recovered was remarkably lower, never exceeding 21%. The deviations observed between the parallel experiments were in general low.

3.2.3. Leaching potential of NP

TCLP is used by the U.S. EPA for the determination of the mobility of contaminants present in wastes. The method simulates leaching from a landfill under a mismanagement scenario (unlined landfill). By following a similar protocol, the leaching potential of the residual NP was determined for each of the amended soils after the incubation period. The risk from leaching appeared to be appreciable low. The highest amount of mobile NP was observed in limed sludge (Fig. 2b). Nevertheless, the amount transported to the aqueous phase in this case still remained below 2% of the applied compound. Polymer conditioning of sludge resulted in a slight decrease of the total amount of mobile NP after 87 d of incubation. The latter was even lower in soils amended with liquid sludge (0.4% of applied NP).

3.2.4. NP degradation products

The combined organic phases obtained from sequential extraction were analyzed by means of HPLC. The radioactivity

Table 1 – Losses of water^a and radiolabelled NP during sludge treatment

| Sludge | Dry matter ^b (%) | NP losses (%) |
|--|-----------------------------|----------------|
| Liquid (LQ) | 4.8 | – |
| [no treatment] | | |
| Centrifuged (CE) | 22 (21–23) | 0.75 (0.7–0.8) |
| Freeze-thawed/centrifuged (FT) | 25 (24–27) | 0.45 (0.4–0.5) |
| FeCl ₃ conditioned/centrifuged (FE) | 30 (26–31) | 0.44 (0.4–0.5) |
| FeCl ₃ , CaO conditioned/centrifuged (LM) | 39 (36–41) | 1.31 (1.3–1.4) |
| Cationic polymer conditioned/centrifuged (PO) | 28 (27–29) | 0.56 (0.5–0.6) |

a Based on the dry matter of the treated sludges (w/w).

b For dewatered sludges calculated indirectly, based on the mass of water losses (average and range of three parallel experiments).

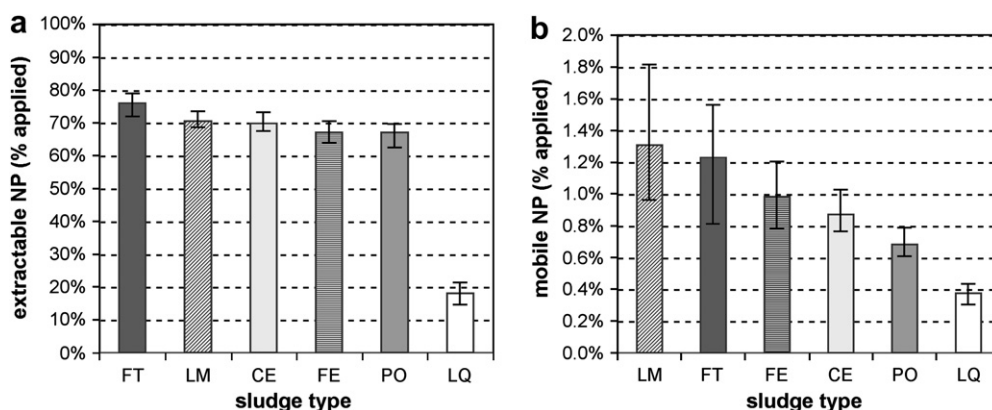


Fig. 2 – Levels of NP extractable by organic solvents (a) and by the leaching-simulation procedure (b) in the incubated soils amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge.

representing NP was subtracted from the total radioactivity of the concentrates, with the resulting values being represented in Fig. 3a. Remaining radioactivity assignable to NP degradation products was much higher in the soils where NP residues were very low, i.e. in soils amended with non-dewatered sludge.

Radioactivity not corresponding to the parent compound but to its degradation products was also quantified in the leaching-simulation extracts. As it appears in Fig. 3b, the soils treated with liquid sludge did not display a high potential for leaching of metabolites/transformation products, although these compounds were present in high amounts in these soils (Fig. 3a). Additionally, it is noteworthy that in some cases the total amount of leachable radioactivity which was not assignable to the parent compound appeared to be even higher than the extractable amount of the latter (Figs. 3b, 2b). Thus degradation of NP may have occurred during the storage of the aqueous leaching-test extracts and before their analysis.

Fig. 4 shows characteristic chromatograms from the analysis of residues extracted from the sludge-amended soils by organic solvents. A peak corresponding to a polar degradation product of NP could be observed in chromatograms related to liquid sludge-amended soils, where degradation of NP was considerably more advanced (Fig. 4a). An additional degradation product of NP was detected, that occurred only when the cationic polymer had been used as sludge-conditioner (Fig. 4c). The respective compound eluted about 2.5 min after the parent compound and represented, 87 d after spiking, an amount equal to 2–3.5% of the applied radioactivity.

Although present in trace amounts, an effort was made to obtain qualitative information about the degradation product detected in PO-amended soils. The extracts from the soils amended with PO or with CE (the latter as a negative control) were applied on preparative HPLC and the relevant fractions were collected, and analyzed using GC/MS (Fig. 5). Although not any significant difference was observed in Full Scan, or even Selected Ion Current (SIC) chromatograms for ions occurring in the mass spectrum of NP, a peak present only in the polymer-related extracts was detected in SIC chromatograms of ions corresponding to a reported degradation product of NP,

the 4-(3,5-dimethyl-3-heptyl)-2-nitrophenol (Telscher et al., 2005). All major ions previously reported for 4-(3,5-dimethyl-3-heptyl)-2-nitrophenol accounted in the Mass Spectrum corresponding to the peak present in extracts obtained from soils amended with polymer conditioned sludge.

3.3. Distribution of radioactivity

The extractable residues were divided into those extractable by acetone, *n*-hexane and methanol during the sequential extraction procedure. The fractionation data were examined after normalization relative to the total amount of extractable residues. The normalized distribution was very similar for soils amended with different sludges (83–88% extractable by acetone, 2–7% by *n*-hexane and 7–12% by methanol, data not shown).

The bound residues were particularly high in LQ systems (57–65%), while not significantly different between CE, FE, PO and LM (22–28%) and slightly lower in the case of FT (18–24%). In contrast with the extractable residues, the influence of the sludge treatment on the normalized distribution of the non-extractable radioactivity was significant (Fig. 6). Binding of NP and possible transformation products seemed to occur preferentially in the humin fraction for all soil-sludge mixtures. Nevertheless, highest binding to the humin was observed for soils amended with limed and liquid sludges. An influence of the various sludge treatments on the distribution of spiked radioactivity between the other fractions of bound residues after incubation was also observed.

4. Discussion

4.1. Elimination of NP during sludge dewatering

Hydrophobic compounds are expected to have a high affinity to sludge organic matter. Ivashechkin et al. (2004) calculated for Bisphenol A (BPA) a partition coefficient, K_d , of 122–201 L/kg ($K_d = C_s/C_w$, C_s , concentration in sludge, C_w : concentration in the liquid phase) for a sludge with the same content of

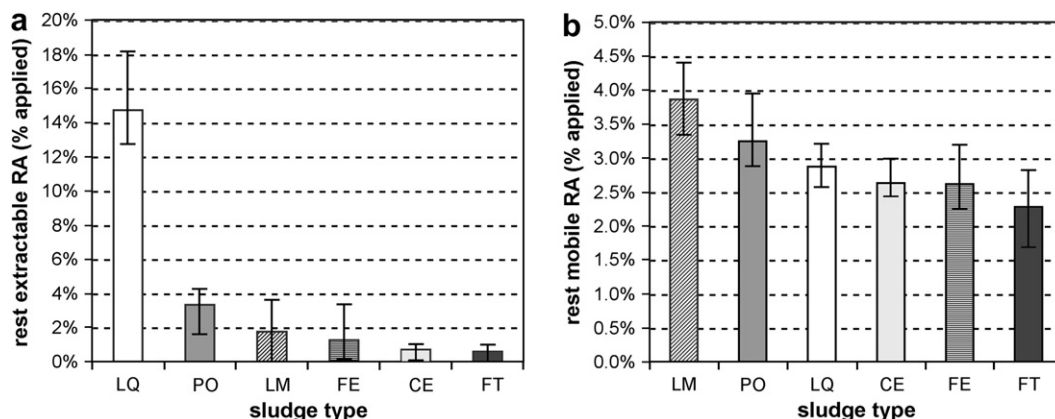


Fig. 3 – Radioactivity (RA) corresponding to degradation products of NP, extracted by organic solvents (a) and by the leaching-simulation procedure (b) from the incubated soils amended with non-conditioned (CE), freeze-thawed (FT), FeCl₃ conditioned (FE), lime and FeCl₃ conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge (averages and ranges of triplicate series).

organic matter as in the present study. Based on the NP losses in the supernatant after centrifugation of the spiked sludges a K_d value of ca. 3000 L/kg can be derived for NP (Table 1, CE). This difference reflects the higher partition coefficient for organic carbon K_{oc} of nonylphenol ($\log K_{oc} = 4.0$ – 5.6 for NP instead of 2.5 – 3.2 for BPA, Ivashechkin et al., 2004), which is also shown by the low leaching potential observed in the sludge-amended soils.

The desorption effect of liming for compounds with $pK_a > 10$ has been predicted by Ivashechkin et al. (2004). The phenomenon, observed for BPA, had been attributed to the deprotonation of those compounds in $pH > 10$, values achieved by liming. The elimination of NP from limed sludge, in the current study, was increased. Nevertheless, the desorption was very low (only 1.3% of the applied amount) in

comparison with the BPA desorption (80%) reported at similar conditions. Nevertheless, elimination data indicate a slightly higher affinity of NP to the water phase of LM.

4.2. Effect of sludge treatment on the fate of sludge-sorbed NP in soil

4.2.1. Effect of dewatering by centrifugation

By comparing the fate of NP in soils amended with liquid sludge and centrifuged sludge, the effect of sludge dewatering could be examined. It must be noticed though that the dry matter amount applied was 10 times less for LQ, since an equal amendment would result in a soil with a water content above the maximum water holding capacity. In practice, since more liquid sludge is needed to cover the same nitrogen needs

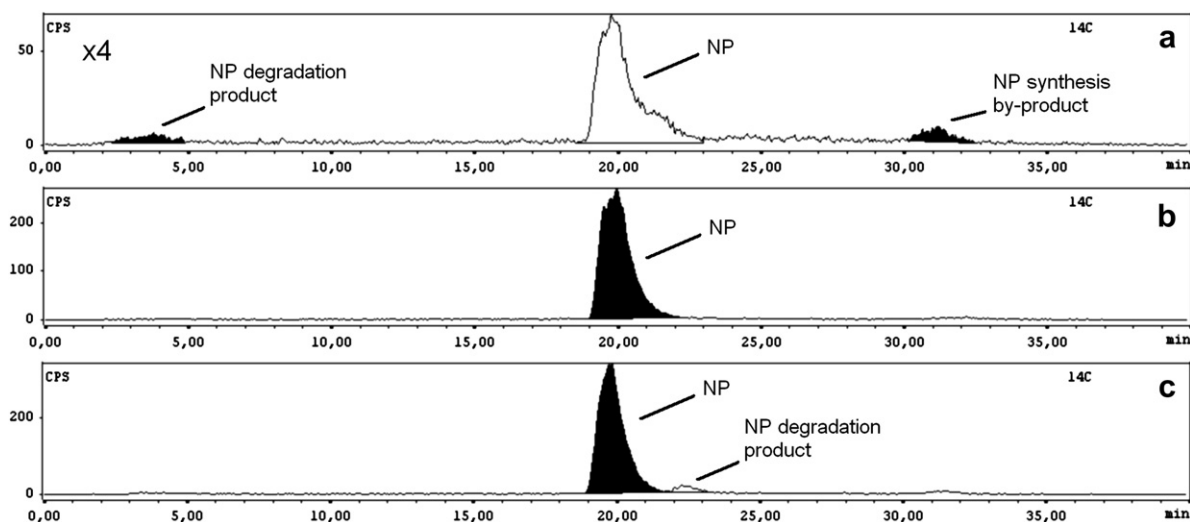


Fig. 4 – Chromatograms of HPLC-radio detection for the organic extracts of soils amended with non-dewatered (LQ) (a), non-conditioned (CE) (b) and polymer conditioned sludge (PO) (c) after 87 d incubation. The peak at $R_t = 20$ min corresponds to NP. The peak at 31 min corresponds to the main by-product of NP synthesis and it was detectable in chromatograms of almost all the extracts (here it can be observed only in (a), which was taken in zoom mode).

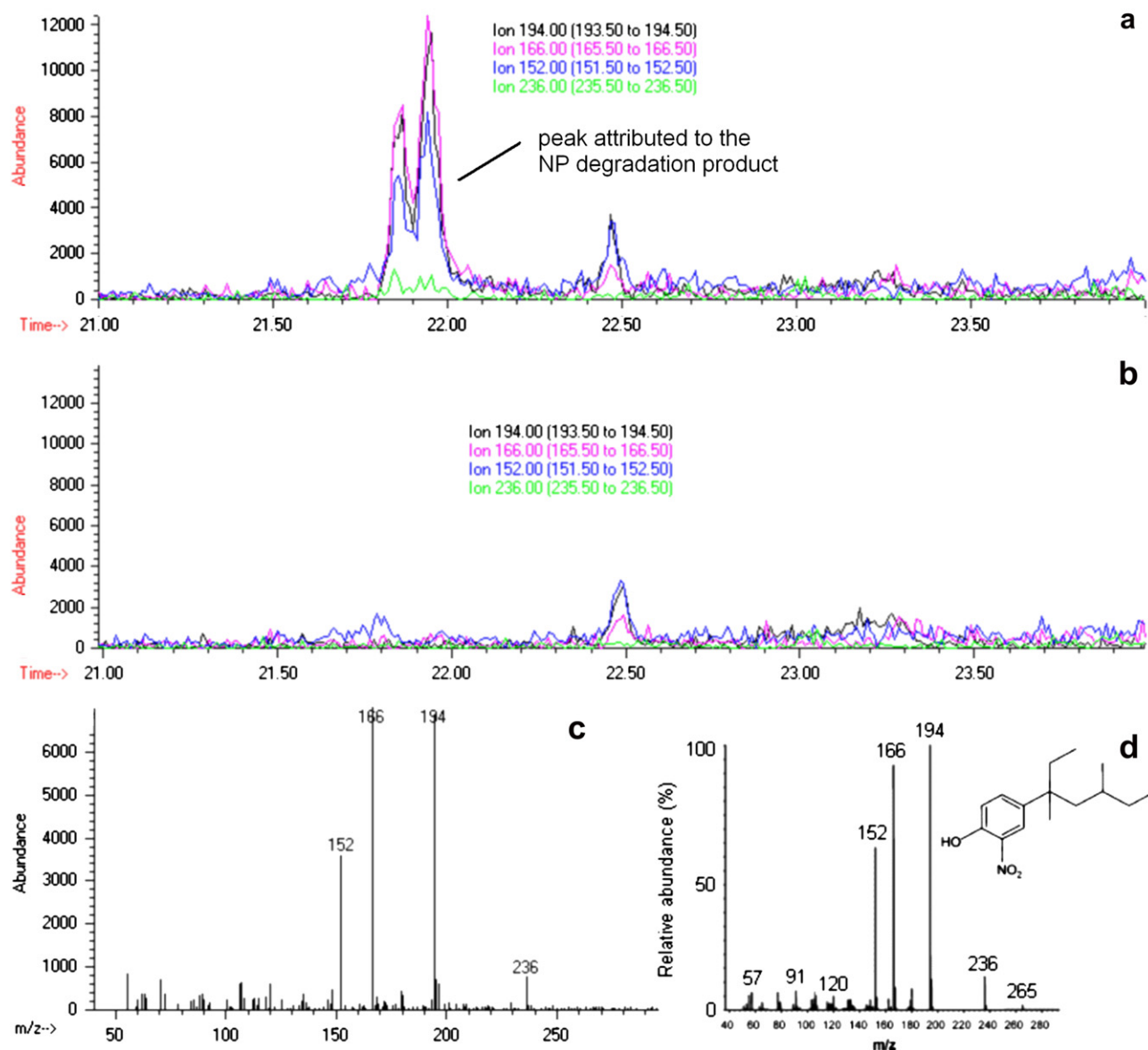


Fig. 5 – Part of the GC/MS(SIC) chromatograms of the HPLC effluent fractions with $R_t = 22$ – 23 min, for extracts of soils amended with polymer conditioned (PO) (a) and non-conditioned sludge (CE) (b). EI-MS of the peak attributed to NP degradation process (c) and comparison with the MS of 4-(3,5-dimethyl-3-heptyl)-2-nitrophenol (d) (Telscher et al., 2005) are shown below.

of crops, the sludge is applied either in doses or in combination with chemical fertilizers. Thus, the scenario of this study can be considered realistic, representing the fate of NP in one of the applied LQ sludge doses except the fact that the addition of fertilizers may affect the fate of NP.

Dewatering of sludge had a negative effect on the degradation rate of NP in amended soils. After incubation in soils amended with CE, the amounts of humin-bound residues, extractable degradation products, and residues bound to humic acids were lower than in soils amended with LQ (by 26%, 14% and 8%, respectively). This resulted in elevated extractable residues of the parent compound (by 52%) in CE samples. The mineralization rate was also lower

than in LQ-amended soils (by 2%), combined with a prolonged lag-period.

The risk of leaching of NP was slightly higher when CE was used, though still quite low. The increase in leaching potential can be attributed to the higher amount of intact NP residues under such conditions. Notwithstanding the leaching-test is not providing evidence for the accumulative leaching, since it was performed after a 3 months incubation period, when significant amounts of the parent compound had already been transformed and sequestered.

For discussing the possible reasons behind the low NP degradation rate in soils amended with CE, the factors of bioavailability, oxygen penetration, microbial populations

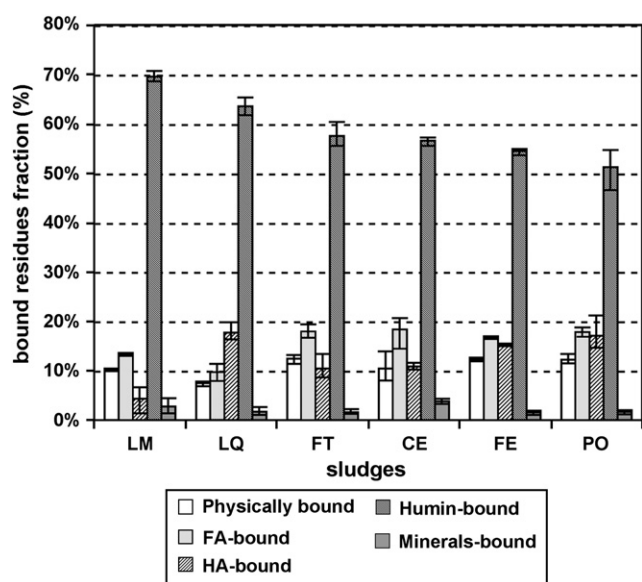


Fig. 6 – Distribution of the bound residues in soils amended with non-conditioned (CE), freeze-thawed (FT), FeCl_3 conditioned (FE), lime and FeCl_3 conditioned (LM), polymer conditioned (PO) and non-dewatered (LQ) sludge after 87 d incubation. The values (averages and ranges of triplicate series) represent fractions of the total bound radioactivity per system.

and total organic carbon need to be considered and compared, for systems amended with CE and LQ.

The bioavailability of an organic compound may be influenced by the availability to the aqueous phase of the soil. Corresponding data were achieved by testing the leaching potential in the present study. Since the water-extractable amount of NP depends also on the total “available” (non-bound) NP, the ratio between water and organic solvents extractable NP may be used as a rough indicator of its availability to the soil aqueous phase. The calculation of this ratio (based on the data presented in the graphs in Fig. 2a and 2) led to the assumption that NP residues were more available to the aqueous phase of soils amended with LQ, at least after the incubation period (ratio 2.0–2.2% for LQ in comparison with 1.1–1.5% for CE). In a previous study, where NP had been spiked on the soil-sludge mixtures, this ratio had been proven to be equal for CE and LQ (Kouloumbos et al., 2008). In the corresponding study, the fate of NP was similar indeed. Thus, centrifugation of LQ already containing NP may decrease the availability of the organic pollutant to the soil aqueous phase. The spiking of NP to soil/sludge system probably lead to a partitioning of NP between soil particles and the surface of sludge aggregates. Hence NP is more available to microorganisms. It is noted that a possible artefact due to degradation of NP in the leaching-test extracts would not affect the syllogism, since the same conclusions were made on the basis of the ratio of total “leachable radioactivity” to organic solvents extractable radioactivity.

The decreased availability of NP in CE could be attributed to an entrapment of NP molecules to remote sites of sludge

aggregates after centrifugation. Further hypothesis is that the presence of dissolved organic matter in LQ may solubilize NP, thus favoring its partition to the aqueous phase in soil. Increased bound residues in the HA fractions of these systems may be related to an increased partitioning to those substances, which are partly removed with the supernatant during centrifugation. A different explanation can be based on the fact that, in the current experiments, the concentration of NP per dry matter of sludge was considerably higher in LQ than in CE (see Section 3.1). The high amount of NP spiked per dry matter in LQ may lead to a saturation of primary adsorption sites and hence a localization in external, more accessible sites in the sludge matter, enhancing the degradation rates of the pollutant.

Hesselsøe et al. (2001) showed that O_2 penetration into sludge aggregates is an important factor for nonylphenol degradation, observing lower diffusion of O_2 and significantly lower degradation in bigger sludge aggregates. Low availability of NP to O_2 may also be responsible for the low biodegradation rates observed in CE in the current study. A prolonged lag-period can be correlated with a slower diffusion of O_2 into CE aggregates.

Effects of sludge treatment, i.e. a negative effect of sludge centrifugation, on microbial populations and species cannot be excluded. Nonetheless, literature provides evidence that bacteria populations rapidly increased after centrifugation of digested sludges (Qi et al., 2007). Furthermore, the amendment of centrifuged sludge in the present study corresponded to an increased amount of total organic matter (although dissolved organic matter, which is easily assimilable, has been removed after centrifugation) and presumably of nutrients as well. Consequently, the total microbial activity should not be decreased in CE. In addition, significant changes in the proportions of different bacterial groups during sludge dewatering are not expected either (Vilanova and Blanch, 2005).

On the other hand, the difference in the moisture levels of soils amended with CE and LQ (65% and 73% of WHC respectively, see Section 2.3) was shown not to have been a critical factor in causing the increasing persistence in CE-amended soil, on the basis of an additional incubation experiment carried out. By the corresponding experiment, increased persistence of NP in dewatered sludge was a fact also when moisture of liquid and dewatered sludge-amended soils was set to the same level (data not shown).

4.2.2. Effect of freeze-thaw conditioning

The amendments of CE and FT originated from treatment of the same amount of liquid sludge, meaning that they correspond to an equal amount of sludge dry matter before dewatering. Therefore, their comparison is performed on this basis and not on that of the nutrients, such as nitrogen, supply to the crops. The same applies for the investigation on the other conditioning treatments.

Three months after the amendment, the levels of extractable NP were slightly increased (on average by 6%) in FT, while correspondingly a decrease in mineralization (av. by 2.3%) and humin-bound residues (av. by 2.1%) was observed. The most obvious contrast in the fate of NP was observed for the mineralization rates. No significant differences were observed in the bound residues distribution or in NP leaching potential.

Effects of freeze-thawing on the availability of NP and O₂ to microorganisms, as well as on sludge endogenous consortia, are both possible. Freeze-thawing in comparison with other conditioning processes is known to produce less permeable sludge flocs with short pores, and smooth pore surface (Martel, 2000; Chung et al., 2003; Chu and Lee, 2004). Besides, freeze-thawing of sludge has been reported to reduce the number of pathogens significantly, depending on the strain or the type of bacteria and the freeze-thawing conditions (Chu et al., 1999). That can be either due to osmotic effects (predominating in slow cooling) or due to intracellular freezing (fast cooling) (Sanin et al., 1994).

When NP was spiked in a mixture of soil and freeze-thaw conditioned sludge, the extractable NP after incubation was considerably higher and the mineralized portion lower, in comparison with a mixture containing simply centrifuged sludge (Kouloumbos et al., 2008). The spiking strategy of the aforementioned study must have resulted in a distribution of NP to soil and sludge particles, while due to centrifugation before spiking no sequestration effect is expected. However, since the NP degradation rate was lower in that case as well, freeze-thawing seems to predominantly affect the fate of NP by influencing the biological activity of the sludge-amended soil.

4.2.3. Effect of lime conditioning

Liming of sludge did not have any influence on the residual amount of extractable NP three months after fertilization. Nevertheless, the transformation pathway was different to that in soils amended with non-conditioned sludge. More specifically, binding was considerably more important than mineralization, the latter being negligible. Higher binding occurred particularly in the humin fraction of the soil-sludge mixtures. The leaching potential of NP residues increased when lime was used.

Although decreased mineralization rates were observed also when spiking was performed on the soil-sludge mixture (Kouloumbos et al., 2008), liming of sludge in the mentioned study led additionally to significantly higher amounts of residual extractable NP in comparison with non-conditioned sludge. In that study, an adverse effect of lime on populations of microorganisms was assumed. It is possible that in the current study sequestration of NP in centrifuged, as well as in limed/centrifuged sludge, was a determinant factor, delaying its degradation rate, independently of any effects on the microbial populations. In the previous study, where NP was more available, the latter was degraded at rates which were governed by the amount and/or type of microorganisms, i.e. faster in CE-amended soils, where no negative effects in the degrading species occurred. It is known that liming adversely affects microbial populations in sludge (Leclerc and Brouzes, 1973) and can be used as an efficient disinfection method.

Since in practice NP will enter the soil system as a component of centrifuged sludge, the impact of liming observed in the current study, namely a change in the transformation route rather than change in degradation rates, is expected to occur. The mechanism behind this phenomenon may include a fast binding of metabolites such as organic acids, favoured by the higher pH (6.7 in comparison with 6.3, measured for all the other systems), thus preventing their further decomposition

and mineralization. Besides, consortia able to completely metabolize NP into CO₂ may be missing. If such bacteria originate from sewage sludge, then an effect due to the high pH value reached during liming (ca. 11) can be assumed. In case soil species play the predominant role in NP mineralization, the impact of high pH of the amended biosolids on soil consortia may also be observed.

The increased NP leaching potential in LM-amended soils can be attributed to the high pH of the respective biosolids, fostering deprotonation of the model pollutant. The ratio “leachable” to extractable NP was increased in LM systems, indicating higher solubility to the aqueous phase, as foreseen anyway by the increased elimination of NP during centrifugation of limed sludge. That was not the case when NP had been spiked on the soil-sludge mixture (Kouloumbos et al., 2008), whereby the high leaching potential was attributed to the increased amounts of extractable NP residues.

4.2.4. Effect of polymer conditioning

Prior conditioning of the amended sludge with cationic polymer was related to an increase in the amount of the extractable degradation products and a decrease in the amount of the produced ¹⁴CO₂. More accurately, the former appeared to be exclusively due to the production of a nitrophenol derivative, while mineralization rates gradually decreased as the incubation time elapsed.

Interestingly, a similar effect on the mineralization process was perceived in the previous study (Kouloumbos et al., 2008). In contrast, the nitro-alkylphenol reported here did not belong to the findings of the former study. Thus, the possibility that formation of the nitro-product is a precursor to the decreased mineralization of NP is not strongly supported.

Chu et al. (2003) observed a decrease in methane production in prolonged stages of the anaerobic digestion process for activated sludge that was beforehand flocculated with a cationic polymer. In that study, microphotographic data revealed greater floc size and denser structures for the polymer-conditioned sludge. It is possible that a similar effect of polymer conditioning occurred in the current study. At the first stages of the incubation of amended soils the microorganisms would degrade the loose surface of the sludge flocs with adsorbed NP, but reaching the denser cores of the sludge aggregates, the process and the mineralization rate slows down. The availability of NP to water was found to be slightly lower in PO than in CE after the incubation of soil-sludge mixtures, thus supporting the above hypothesis of NP being not easily assimilable in the core of polymer conditioned sludge aggregates.

Formation of the nitrophenol may be a result of the decomposition of the polymer agent based on polyacrylamide. The polymer is readily biodegradable in the environment (NER-OLAN Wassertechnik GmbH, 2005), while it produces nitrogen oxides after thermal decomposition. It has to be noted, however, that the possibility of an artefact, i.e. the formation of the nitrophenol during handling of the soil extracts by rotary-evaporation can be excluded on the basis of respective tests performed in the frame of the current study (data not shown). Nitrophenols are in general highly toxic compounds, as well as less biodegradable than phenols (Leung et al., 1997), thus their presence in soils may pose risks to the

environment. However, the nitro-compound detected in this study was produced in low amounts in the corresponding incubated soils. While the exact conditions that favoured its formation in PO-amended soils need still to be clarified.

As mentioned before, Telscher et al. (2005) also detected 4-(3,5-dimethyl-3-heptyl)-2-nitrophenol in incubated soil-sewage sludge mixtures containing NP. In that study, sampled sewage sludge was already dewatered and originated from the same wastewater treatment plant (WWTP) as the sludge used in the present study. In this WWTP, NEROLAN CE 679 S polymer is applied for conditioning the digested sludge before mechanical dewatering by centrifugation. This fact supports the assumption that in the study of Telscher et al. (2005) the formation of the nitro-substituted nonylphenol was driven by the presence of the specific polymer in the sewage sludge and not by any other chemical or biological component of the studied systems.

4.2.5. Effect of ferric chloride conditioning

Chemical conditioning of sludge by FeCl_3 in doses normally used in practice did not affect the fate of NP in sludge-amended soils. A slight enhancement of residues bound to humic acids in comparison to those bound to the humin fraction was the only significant difference observed, together with a shorter lag-period in mineralization.

5. Conclusions

The correlation between commonly applied sewage sludge conditioning and dewatering techniques and the fate of organic pollutants in sludge-amended soils were investigated. The applied methodology involved application of different sludge treatment techniques on the same precursor sludge, spiked with the model compound p353-nonylphenol before sludge processing.

For the soil and sludge used and the model compound NP the results indicated:

- a major impact of sludge centrifugation, leading to a considerably increased persistence of NP in soil (significantly lower degradation and slightly lower mineralization rates)
- a moderate impact of freeze-thaw conditioning, leading to a modest increase on the persistence of NP in soil (significantly lower mineralization and slightly lower degradation rates)
- a minor effect of sludge liming, enhancing the formation of bound residues in soil with a concomitant lower mineralization rate of NP, as well as a slight increase in NP leaching potential
- a minor effect of conditioning by an acrylamide-based cationic polymer, expressed as lower mineralization rates for prolonged incubation periods, the occurrence of a nitro-addition product of NP, as well as a slightly lower leaching potential of NP
- a negligible impact of ferric chloride conditioning on the fate of NP in soil.

Analysis of the data highlighted the importance of the role of physicochemical factors of treated sludge on the fate of

organic pollutants in soil, such as the concentration in the water phase, the oxygen supply or the local concentration rather than an impact of sludge treatment on microbial populations. Nevertheless, a deeper interpretation of the observed effects would be necessary for assessing the potential behavior of other organic pollutants in the presence of different sludge or soil matrices or under different conditions.

Future studies on this topic should examine the roles of various sludge physicochemical properties and that of its microbial content individually. Special attention should be also given on the spiking strategy. Spiking of artificial pollutants should optimally be performed before sludge stabilization or even on the wastewater before its treatment, since adsorption of the pollutants to wastewater components may influence their fate during further sludge treatment. Finally, external factors, such as natural freeze-thawing cycles of soil or the growth of plants may interfere with the here observed effects of sludge treatment on the fate of organics in sludge-amended soils.

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